

# Effectiveness of an Open Limestone Channel in Treating Acid Sulfate Soil Drainage

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**Abstract** An open limestone channel (OLC) was constructed within an existing drain to treat the acidic and metal-rich drainage waters generated from an acid sulfate soil (ASS) catchment. The OLC was constructed downstream of a catchment pump and it consisted of a series of ponds and limestone sections. The accumulation of sediment over the limestone, preventing contact of limestone with acidic water, was the greatest problem impacting the OLC in its first year of operation. The continuous or sporadic operation of the catchment pump (at 120 l/s) was not sufficient to flush sediment from the limestone. The accumulation of large amounts of sediment onto the limestone reduced the amount of alkalinity and

calcium released into solution. However, if the sediment is removed by agitating the limestone then an equivalent or greater amount of alkalinity may be added to solution and more metals removed from solution compared to fresh limestone. The coating on the limestone had a high concentration of manganese oxides in addition to slightly lower concentrations of aluminium and iron. Removal of these metals from the water was due to the increase in pH produced by limestone dissolution in addition to sorption reactions of the existing coating which had natural microbial activity.

**Keywords** Acid sulfate soils ·  
Open limestone channel · Passive acidity treatment ·  
Changes in limestone surface mineralogy

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## 1 Introduction

### 1.1 Acid Sulfate Soils

Acid sulfate soils (ASS) have devastating environmental and social impacts due to acidic and metal-rich drainage that is produced. Some of these impacts include fish kills, corrosion, loss of biodiversity, subsidence and loss in agriculture productivity (White et al. 1996; Melville and White 2002). ASS are characterised by iron sulfides, typically pyrite and its oxidation products, that are present in the soil. Upon exposure to oxygen the pyrite is oxidised releasing

iron, sulfate and hydrogen acidity. The acidic conditions can also dissolve other minerals in the soil and release metals such as aluminium, zinc or copper (van Breemen 1993). After periods of rainfall this acidic metal-rich pore water solution may be discharged into waterways (Willett et al. 1993).

Iron monosulfide rich sediment (or ‘monosulfidic black ooze, MBO’; Sullivan and Bush 1999) may form at the base of many waterways or drains within ASS catchments. The formation of iron monosulfides occurs under reducing conditions with organic matter and dissolved sulfate and ferrous iron present in the water column, or through the reduction of precipitated iron oxyhydroxides at the sediment-water interface (Smith 2002). These iron monosulfides are an important process in the capture of dissolved metals from drainage water, however they are unstable and can consume oxygen when ferrous iron is oxidised (Sullivan and Bush 1999) potentially generating further acidity through iron hydrolysis.

## 1.2 Management

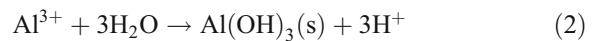
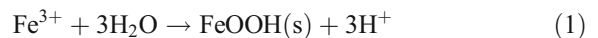
In Australia, primary industries such as the sugar and dairy industries utilise ASS for production. These primary industries do not have the resources, due to a decline in commodity prices, to invest in large capital solutions favoured by the mining industry to treat and manage the acid discharge problem. Management of ASSs and improvements of the discharge water quality have been typically achieved by low cost land management options. These techniques include sea-water neutralisation via flap gate management, laser levelling, hill planting, soil liming and drain management (Blunden et al. 1999; Aaso et al. 2002; Green 2005). Land management techniques are an essential long term requirement to minimise pyrite oxidation and the export of acidity present in the soil. These strategies focus on targeting the acidity along the hydrological pathway from the soil profile to the discharge point into the estuary.

The acidity already present in the catchment, or that which cannot be prevented from being transported from the catchment through land management, needs to be neutralised. Many innovative systems are available (e.g., permeable reactive barriers, aerobic and anaerobic wetlands (Waite et al. 2002)) however, in this study, we focus on a limestone system that is of low cost and has low maintenance. A system

developed to treat acid rock drainage (ARD) and referred to as an open limestone channel (OLC) has been adapted and used within an ASS catchment.

## 1.3 The Open Limestone Channel

Open limestone channels (OLCs) are constructed by placing limestone boulders into a sloping waterway (Ziemkiewicz et al. 1997; Rose and Lourenso 2000). Typically a slope of greater than 20% is recommended to reduce the accumulation of sediment and precipitates, particularly iron ( $\alpha$ -FeOOH, Eq. 1) and aluminium [ $\text{Al}(\text{OH})_3$ , Eq. 2], onto the limestone which may reduce permeability and reactivity (referred to as ‘armouring’; Ziemkiewicz et al. 1997).



This investigation into a modified OLC constructed in an ASS landscape will:

- determine if dissolved metals are removed and pH is increased;
- determine the performance of the modified OLC after a coating has developed on the limestone; and
- determine the characteristics of the coating that forms on the limestone.

Understanding the performance of the modified OLC in this environment will improve understanding of limestone neutralising systems that may be used in future applications.

## 2 Materials and Methods

### 2.1 Location

McLeods Creek is a right bank tributary of the Tweed River, located in far north NSW Australia, between the towns of Murwillumbah and Tweed Heads. The average rainfall is 1,752 mm (recorded at a Bureau of Meteorology Station at Murwillumbah Taleswood from 1967 to 2002), however in 2002 the region experienced drought and the average rainfall for the year was 1,015 mm. Most rainfall occurs in or near the summer months (typically November to April).

Occasionally during large rainfall events the flap gates separating the sub-catchment study site from the rest of McLeods Creek and the Tweed River are overtopped. Saline tidal water from the Tweed River may also occasionally enter this drain due to overtopping or blockage of flap gates with debris. The water level within the sub-catchment is controlled by an outlet pump that is automatically triggered to begin operation via a water depth sensor. The modified OLC was constructed within an open ditch drain at the egress point from the 100 ha sugar cane farm which is a sub-catchment of McLeods Creek (28°17' S, 153°30' E). The catchment pump is located directly upstream from the OLC (Fig. 1).

## 2.2 Design

### 2.2.1 Existing Infrastructure

Due to the low topography of the land (less than ~1 m above mean sea level) a catchment pump is essential for discharging water during periods of large rainfall. The modified OLC was built directly downstream from the catchment pump because it was anticipated that the fast flowing water generated from the catchment pump (at 120 l/s) would periodically flush precipitates and sediment that had collected on the limestone. The pump also aerates the water and assists in promoting metal hydrolysis, in particular the conversion of ferrous iron to ferric iron, which rapidly hydrolyzes and precipitates over a wide range of pH (Eq. 1).

### 2.2.2 Specifications

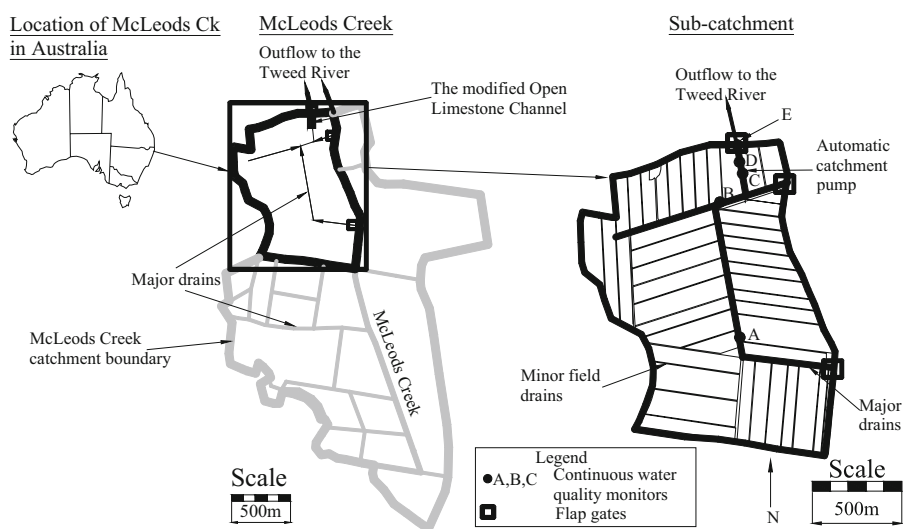
The size of the passive treatment system was limited to fit into the existing outlet drain (about 120 m long) and thereby there would be no loss in available land for sugar cane farming. It was important that the existing flow regime was not impacted because extended periods of water retention on the land could reduce the sugar cane growth due to waterlogged roots (Rudd and Chardon 1977).

The system constructed focused towards treatment of low water flows because it was recognised that the large water flows that occur during flooding could not be adequately treated with a passive system. During large rainfall events acidity and metal weathering products that are flushed from the soil profile into the discharge waters are diluted by rainfall. The OLC is design to treat the first flush and recession water discharges which contain significant quantities of acidity and mineral weathering products and are most problematic (Green et al. 2006).

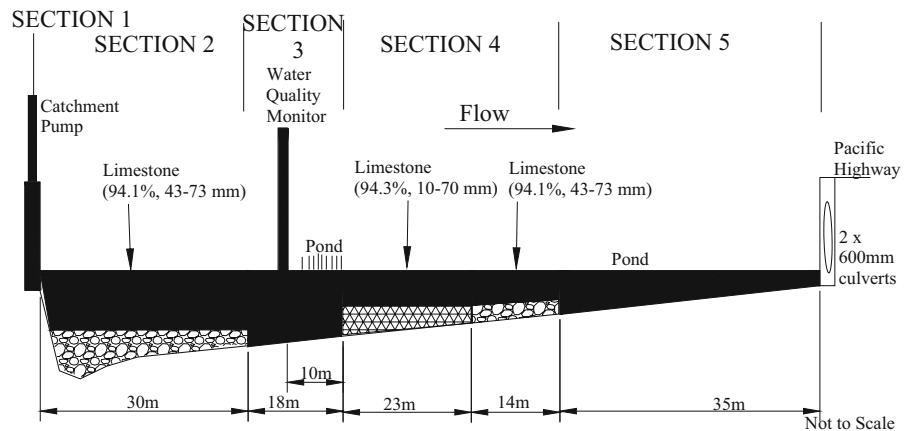
The limestone was placed in the OLC so that it was constantly beneath the water surface. This would allow the ferric and aluminium oxyhydroxides, that may precipitate, to remain suspended in solution (Ziemkiewicz et al. 1996) rather than harden onto the limestone. The OLC varied from typical designs because water was supplied by the catchment pump rather than by gravity flow, and by the inclusions of two settlement ponds (Fig. 2).

It was constructed with 149 tonnes of limestone and it is capable of treating discharge with the mean

**Fig. 1** Location of the McLeods Creek sub-catchment and the modified open limestone channel



**Fig. 2** Diagram of the modified open limestone channel



acidity (of 50.2 mg/l  $\text{CaCO}_3$ ) that had been pumped downstream (at 120 l/s) for 40 min a day (assuming a 20 year life of operation, 94.1%  $\text{CaCO}_3$  and 75% limestone dissolution; see Skousen (1991) for methodology). It was constructed in the following three stages:

1. Removal of iron monosulfide-rich sediment (10 September 2001);
2. Placement of section 2 limestone (1 October 2001); and
3. Placement of section 4 limestone and the pond (14 December 2001).

### 2.2.3 Stage 1. Removal of Iron Monosulfide-Rich Sediment

Prior to construction of the modified OLC the field drain was excavated to remove the iron monosulfide rich sediment that had accumulated at the base of the drain. The sediment was placed onto the adjacent land and on the banks of the drain, mixed with lime and allowed to dry. The removal of the iron monosulfide-rich sediment and the increase in height of the drain banks ensured that the capacity to retain water in the drain was not reduced by the emplacement of limestone.

### 2.2.4 Stage 2. Placement of Section 2 Limestone

Thirty-three tonnes of limestone aggregate (43–73 mm) were placed directly downstream of the catchment pump. The limestone was supplied by DML Lime located near Warwick in Queensland and was 94.1%  $\text{CaCO}_3$ . It was placed at approximately

0.3 m depth from the bottom of the drainage channel over a distance of 30 m. A greater depth of limestone was placed directly adjacent the catchment pump to reduce the impact of erosion on the drain bottom. The limestone placement will offset some of the decrease in pH induced by catchment pump aeration and metal hydrolysis.

### 2.2.5 Stage 3. Placement of Section 4 Limestone and the Ponds

A settling pond was constructed after the section 2 limestone, to collect precipitates that are suspended in the water. The pond consisted of an 8 m length of channel, a water quality metre followed by 10 m of artificial sea grass. The artificial sea grass (representing in density and stiffness *Posidonia Australis*; Wallace 2003) floated in the water column and was placed to collect precipitates. It was constructed by attaching strips of polypropylene plastic to a metal grid. PVC pipes of various diameters were also placed vertically into the soil to baffle the flow. Real wetland plants were not used due to the high water levels, the variable water quality (pH 4.0–6.3, the possible obstruction to water flow, and the difficulty in establishment as it is a major drain that always contained water.

Subsequent sections of limestone buffered the decrease in pH due to dissolved metal precipitation in the pond. In total 23 m and 27.2 tonnes (10–70 mm) of 94.3%  $\text{CaCO}_3$  limestone was placed after the pond. This was followed by 14 m and 88.6 tonnes (43–73 mm) of 94.1% limestone. The depth of limestone was approximately 0.3 m in the centre of the drain and the width of the channel was approximately 4 m.

The final stage of this system consisted of a 35 m section of the original drainage channel without any limestone. This section of the drainage channel is shallow (commonly 0.3 m) and natural vegetation had established in the drain to act as a final filter to the water.

## 2.3 Analytical Techniques

### 2.3.1 Water Quality

The performance of the modified OLC was monitored with constant measurement (15 min but averaged over the day) of pH, electrical conductivity (EC) and temperature (TPS WP-81 water quality unit) within and upstream of the OLC. The probes were cleaned and TPS WP-81 was recalibrated every 2 weeks according to the manufacturer's instructions.

### 2.3.2 Precipitate Analysis

Limestone samples were collected randomly from the OLC and the precipitates that collected on the surfaces were analysed. The coating on air-dried limestone was removed using a plastic spatular and further dried in an oven then grounded for analysis by X-ray diffraction (XRD) and secondary ion mass spectrometry (SIMS). Scanning electron microscopy (SEM) analysis was conducted on the limestone coating after it had been removed from the limestone using a sticky carbon strip which was then carbon coated.

### 2.3.3 Limestone Reactivity

The reactivity of limestone from the modified OLC was compared to fresh limestone by placing the rocks into separate beakers of acidic water from the drain. The experiment was conducted within several hours of limestone collection to prevent the coating on the limestone from hardening and the water chemistry of the drain water from changing. Fresh limestone from the same batch used within the modified OLC was rinsed first with deionised water to remove any fine limestone powder.

Cation samples were collected from a stirred solution, with the limestone removed, when the solution pH was steady and no longer increased. Samples were collected in acid washed bottles, chilled and acidified (pH <2 conc HNO<sub>3</sub>) directly after

collection. Some samples were filtered through a 0.45 µm membrane to measure the dissolved species concentration. Cation and sulfur concentrations were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). All sulfur detected by ICP-AES was assumed to be present as sulfate. Those samples not filtered were used to measure the total species concentration (particulate + dissolved). Acid digestion was undertaken (APHA 1998, Method 3030D) if the turbidity was less than 1 NTU (nephelometric turbidity unit). Dissolved ferrous iron was measured directly after sample collection using the 1,10 phenanthroline method with a portable spectrophotometer (wavelength 510 nm) and powder pillows (HACH: Method 8146). Alkalinity titrations were undertaken within 24 h of sample collection by the addition of HCl to end point pH 4.5, as specified in APHA (1998; Method 2320). Grab samples were also collected from the modified OLC and analysed in a similar manner for water quality parameters.

## 3 Results

The daily discharge in January and April 2002 met the criteria of 40 min a day of pumping on 59 days over this period (i.e. 49% of the time). Less rainfall occurred in the period from May to November and it is expected that a similar number of days or more had 40 min a day of pumping or less.

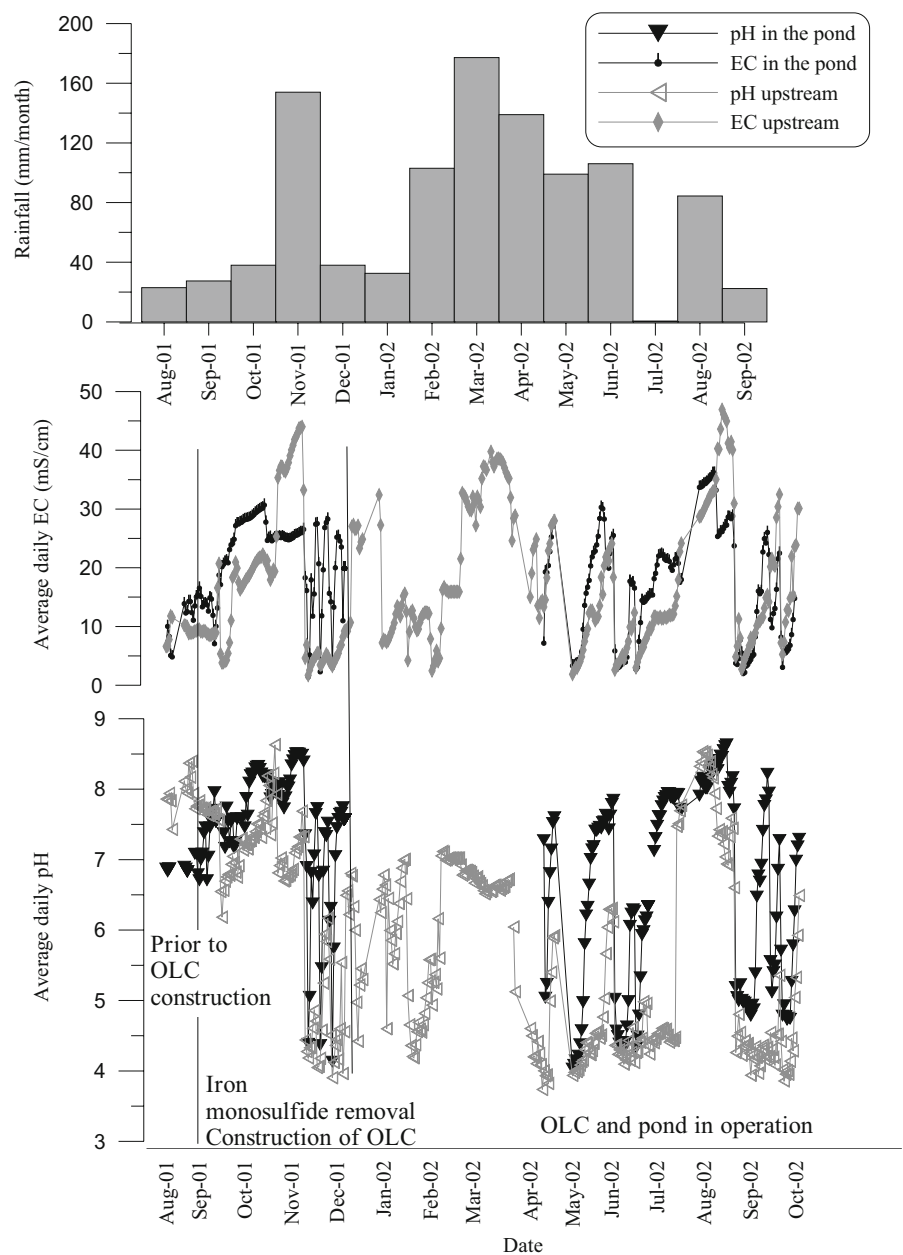
### 3.1 Water Quality

The overall trend from January to August 2002 was that in the modified OLC pH was greater than upstream in the catchment (Fig. 3). This is most likely due to the limestone in the modified OLC, however saline water neutralisation due to a downstream leaking flap gate must also be considered. Large fluctuations in EC, upstream and downstream of the modified OLC (separated with a concrete wall at the catchment pump), does indicate that the flap gates were leaking and there was penetration of salt water into the drain (particularly at the start of August 2002).

### 3.2 Precipitate Analysis

In February 2002 (which was 2 months after complete construction of the modified OLC) a thin green

**Fig. 3** The variation of pH and electrical conductivity upstream of the modified open limestone channel (at monitor B in Fig. 1) and within the first pond (monitor D in Fig. 1). The rainfall each month was measured at Murwillumbah (Taleswood) by the Bureau of Meteorology. Breaks exist in some of the continuously monitored variables because of power failures at the site caused by lightning storms



coating (possibly microorganism growth) had developed over the surface of the limestone. This coating was amorphous to XRD and only calcite, quartz, feldspar and kaolin type mineral were detected. These silicate minerals could be limestone impurities or soil particles.

In June the green coating appeared to be more prominent on the upward facing surface of the limestone. On the opposite side of the limestone (facing the bottom of the drain) a black coating was

apparent. The only minerals detected by XRD were associated with the limestone impurities, sediment from soil transported downstream, or drying of the sample. Hence SEM analysis was conducted to determine those minerals that are amorphous to XRD. The side of the limestone facing the bottom of the drain was found to contain significant concentrations (10–30%) of manganese compared to trace concentrations (<3%) on the upward facing surface of the rock (Table 1). Measurable iron concentrations

**Table 1** Characteristics of the coatings that formed on the limestone in the modified open limestone channel

Month the rock was collected	June 2002		November 2002			
	Facing the surface	Facing the bottom	Facing the surface		Facing the bottom	
Method of analysis	SEM <sup>a</sup>	SEM	SEM	SIMS	SEM	SIMS
O	H	H	H	H	H	H
Mg	T	nil	T	T	T	T
Al	T	T	L	L	L	L
Si	L	L	M	L	T	L
S	T	nil	T	T	T	T
K	Nil	T	T	nil	nil	nil
Ca	M	L	T	T	M	T
Mn	T	M	T	nil	M	T
Fe	T	L	T	T	T	T
Cl	T	L	M	T	L	T
C	–	–	–	H	–	M
N	Nil	nil	nil	L	nil	T
Na	Nil	nil	nil	T	nil	T

<sup>a</sup> Where: *H* is high (>30%), *M* is medium (10–30%), *L* is low (3–10%) and *T* is trace (< 3%) concentrations. Elements that were not examined are marked with ‘–’.

(3–10%) were found on the bottom facing side of the limestone compared with trace quantities on the upward facing side of the limestone. Traces of aluminium were found on both sides.

In August, large amounts of sediment had collected around the limestone and the green coating was less prominent. The sediment was removed for analysis by lightly rinsing the rock with deionised water. However, the remaining black spotting on the limestone could not be removed by rinsing. Once the sediment was rinsed off the remaining coating on the limestone contained gypsum (CaSO<sub>4</sub>) and anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>) in addition to other silicate minerals. The sediment coating that was rinsed off contained hematite (Fe<sub>2</sub>O<sub>3</sub>) and halloysite [Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>] in addition to silicates. The formation of hematite is probably due to suspended soil particles transported downstream although ferrihydrite can be transformed to hematite via dehydration and re-crystallisation (Liu et al. 2005). The gypsum that was detected may have formed when sulfate concentrations were high in the modified OLC.

In November the limestone had a greater cover of sediment over the surface compared to that found in August. The coating on the limestone aggregate that lay below the sediment layer was analysed rather than that on the top layer of rocks that were covered in sediment. This sub-surface limestone had a predom-

inately black staining but there was also orange staining and some green algal growth. There may have been some X-ray amorphous material on the bottom facing side of the limestone because XRD only detected impurities of the limestone, halite and sediment that had collected on the limestone. SEM and SIMS analysis indicated there were trace concentrations (<3%) of iron on both sides of the rock. Trace concentrations of aluminium were found in June, however in November there was more aluminium and low concentrations (3–10%) were found. Greater manganese concentrations were found on the side facing the bottom of the drain compared to the surface. Limestone facing the bottom of the drain may have greater manganese concentrations due to high pH created in the limestone voids. The trace sulfur concentrations may be due to gypsum or metal oxyhydroxide sulfates precipitates. The limestone from the modified OLC in November was viewed under the microscope and a high density of micro-algae was found.

### 3.3 Limestone Reactivity

Laboratory experiments were conducted with limestone from the modified OLC and acidic drain water to determine the removal of dissolved metals from the water. This was compared to a simultaneous experi-

ment conducted for approximately an hour with fresh limestone and the acidic water. To determine the natural change in water chemistry with time during the experiment a standard solution of drain water was also monitored during the length of the experiment. Analytical errors have been addressed in this section by analysis of the difference in concentration between species in the water sample collected and preserved in the field, compared to the aged sample (control) that was analysed at completion of the experiment. The difference in concentrations was the analytical error and if this difference was also found in comparing water from the solutions with limestone then no significant difference could be reported. In most experiments (except in June) the limestone was totally immersed into a controlled volume of water. The weight and shape of the limestone samples were similar.

### 3.3.1 Limestone from the Modified OLC in June

The largest decrease in total and dissolved aluminium in bathing water occurred with fresh limestone (Table 2). The calcium concentration of the water with fresh limestone added was slightly greater, however the difference is close to the analytical error (i.e. 7 mg/l). When limestone from the modified OLC was added to acidic water it caused large decreases in dissolved iron and ferrous iron but an increase in total iron. This increase in total iron is probably due to the ferric iron that had precipitated or the release of ferric oxyhydroxides from the limestone surface when it was placed in the water (Table 3). Manganese also exhibited the largest decrease in water with limestone from the modified OLC.

### 3.3.2 Limestone from the Modified OLC in July

In July the concentration of aluminium, manganese and iron removed from the water containing lime-

stone from the modified OLC was greater than observed for water with fresh limestone (Table 4). However, the aluminium concentration difference is within the analytical error (0.35 mg/l) of the sample collected from the drain compared to the water sample analysed at the end of this experiment. The OLC limestone also resulted in a slightly greater release of calcium and bicarbonate to solution.

### 3.3.3 Limestone from the Modified OLC in November

In November limestone from the modified OLC with and without the sediment coating (removed by shaking the rock by hand in the water) was reacted with acidic drain water. The greatest aluminium removal from the water occurred with limestone from the modified OLC with the original sediment coating retained (Table 5). This result is not certain due to the aluminium concentrations being close and within the analytical error margin (0.11 mg/l). The limestone with the coating shaken off removed the most iron and manganese during the experiment. It also added the most alkalinity to the water. There was a large analytical error for sulfate concentrations and therefore this result is not reported. The increase in calcium concentration was similar in the solutions with fresh limestone and the limestone with the coating shaken off.

## 4 Discussion

### 4.1 Sediment Accumulation

In the initial months after the ponds were constructed, precipitates collected on the artificial sea grass. After 11 months the sea grass was not as effective in precipitate collection because natural drain vegetation had grown in the pond and the precipitates that had already formed on the plastic made it heavier and less buoyant.

**Table 2** Comparison of the dissolved water chemistry from a sample that: (1) had been preserved and measured on site (pH=4.09); (2) fresh limestone had been added; (3) modified open

Sample	Weight of rock (g)	Na	SO <sub>4</sub> <sup>-2</sup>	Mg	Ca	Fe	Mn	Al	K	Fe <sup>+2</sup>
Original water sample (pH=4.4)		1,340	1,460	268	112	0.65	2.41	13.4	44	0.66
Fresh limestone added	640	1,310	1,510	272	164	0.12	2.42	0.14	48	0.07
OLC limestone added	583	1,360	1,490	273	156	0.04	1.59	0.26	50	0.06
Original water sample + time		1,310	1,480	272	119	0.33	2.43	14.5	46	0.25

limestone channel limestone had been added; and (4) had been left in a beaker the entire length of the experiment (48 h)



**Table 3** Comparison of the total water chemistry (dissolved + particulate) from a sample that: (1) had been preserved and measured on site (pH=4.09); (2) fresh limestone had been added;

(3) modified open limestone channel limestone had been added; and (4) had been left in a beaker the entire length of the experiment (48 h)

Sample	Weight of rock (g)	Na	SO <sub>4</sub> <sup>-2</sup>	Mg	Ca	Fe	Mn	Al	K
Original water sample (pH=4.4)		1,340	1,460	272	114	0.8	2.41	13.7	44
Fresh limestone added	640	1,310	1,510	272	164	0.26	2.42	3.07	48
OLC limestone added	583	1,380	1,530	278	159	1.08	1.74	6.15	50
Original water sample + time		1,340	1,480	275	119	0.53	2.43	14.9	46

The beaker experiments have indicated that the accumulation of sediment onto the limestone is the largest problem affecting the operation of the modified OLC in McLeods Creek. With time (possibly within the following year) sediment could clog the modified OLC preventing water from flowing through the limestone. The sediment retention within the limestone pores decreases the time-dependent flow and hence the reaction rates. A large stone size (10–70 and 43–73 mm) was used within the modified OLC to increase porosity and reduce blockage of flow due to sediment accumulation. A smaller stone size would have been more reactive (adding alkalinity more rapidly), however the pore size of the limestone bed would have reduced. It is also possible that small stones may be transported downstream during high flows, blocking the downstream culvert.

A method to agitate and periodically remove sediment from the limestone could enhance the performance of the system. This could be undertaken on farms using machinery (as suggested by Rose and Lourenso 2000) but would also require a sediment trap or geotextile across the water flow path to collect the precipitates and prevent them from travelling downstream. The sediment could also be collected by placing a permeable geotextile cover over the limestone. This geotextile could be placed in sections across the channel and periodically shaken and lifted up to remove the sediment. Agitation of the limestone to

remove sediment may also remove micro-organisms, however, re-establishment within a short period should occur (i.e. they established within two months after initial construction).

#### 4.2 Catchment Pump Sediment Removal

The catchment pump (at 120 l/s) did not generate the flow required to flush sediment from the system. A shallower water level in the channel may have been more effective in aiding removal of the sediment. The depth in the channel when the pump is operating constantly is greater than 0.5 m. Under such conditions, the surface water may be moving rapidly, however water at the bottom of the drain, which is potentially the main transporter of sediment, may not have been moving as rapidly.

#### 4.3 Manganese Precipitation

Manganese will not abiotically precipitate as Mn(OH)<sub>2</sub> until the pH exceeds 9. Despite the pH in the McLeods Creek sub-catchment never exceeding 9 a black manganese rich coating was found on the limestone (Table 1). This manganese oxide coating most likely formed due to microbial action. Coprecipitation of manganese oxide can also occur with ferric hydroxide when ferrous iron activity is low and the water is aerated (Hem 1985). Microbial activity was

**Table 4** Comparison of the ion concentration in: (1) the original dissolved water sample (pH=4.59); (2) the dissolved water chemistry when a fresh rock was placed into the water; (3) the dissolved water chemistry when the modified open limestone

channel limestone was placed in the water; and (4) the dissolved water chemistry of the original water sample change during the length of the experiment (67 h)

Sample	Weight of rock (g)	HCO <sub>3</sub> <sup>-</sup>	Na	SO <sub>4</sub> <sup>-2</sup>	Mg	Ca	Fe	Mn	Al	K
Original water sample (pH=3.4)		0	1,805	1,415	337	154	0.14	2.5	9.2	67
Fresh limestone added	392	75.6	1,874	1,560	347	183	0.04	2.48	0.31	78
OLC limestone added	370	82.3	2,035	1,590	371	190	0.01	0.27	0.19	80
Original water sample + time		0	1,799	1,540	337	151	0.10	2.51	8.85	68

**Table 5** Comparison of the ion concentration in: (1) the dissolved water chemistry of the original water sample (pH=4.97); (2) the dissolved water chemistry of the water with fresh limestone added; (3) the dissolved water chemistry when limestone from the modified open limestone channel (OLC),

was added; (4) the dissolved water chemistry when limestone from the modified OLC that had been shaken to remove some of the coating was added; and (5) the change in dissolved water chemistry of the original sample left standing in a beaker during the entire length of the experiment (48 h)

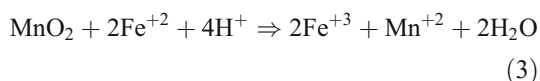
Sample (dissolved)	Weight of rock (g)	HCO <sub>3</sub> <sup>-</sup>	Na	SO <sub>4</sub> <sup>-2</sup>	Mg	Ca	Fe	Mn	Al	K
Original water sample (pH=4.7)		0	3,490	1,800	509	190	0.7	2.12	1.34	110
Fresh limestone added	137	32.2	3,330	1,910	506	210	0.04	2.08	0.14	124
OLC limestone added	139	19	3,850	1,730	548	208	0.05	0.63	0.1	126
OLC limestone added (+ rinsed)	139	48.7	3,680	1,670	528	211	0.02	0.24	0.18	126
Original water sample + time		0	3,470	1,660	490	195	0.05	2.13	1.23	126

obvious within the first 2 months after the complete construction of the modified OLC. All metal oxides that formed on the limestone were amorphous to XRD because the poorly crystalline precipitates would have produced broad diffraction peaks that are difficult to identify by XRD. However SEM and SIMS analysis indicated manganese oxide presence on the limestone.

Brant and Ziemkiewicz (1997) found that limestone with coatings of manganese oxide and microbes performed better in removing manganese than fresh limestone. Despite shorter retention times and lower manganese concentrations this has also been found in this study, particularly when the sediment was removed leaving only the coating that was more firmly attached to the limestone.

The major concerns with manganese oxide precipitates that form in the fluctuating pH conditions of McLeods Creek are:

- manganese oxides are unstable at low pH and may become soluble (Hedin et al. 1994);
- high concentrations of ferrous iron at pH less than or equal to 5.5 may resolublise the manganese oxides (Eq. 3). Sikora et al. (2000) suggested iron concentrations need to be less than 2 mg/l for manganese removal. In this study 17 spot samples were collected from upstream and within the modified OLC. However, the concentration of ferrous iron was less than 2 mg/l and varied from 0.02 to 1.86 mg/l.



(Appelo and Postma 1999);

- adsorbed particles may become remobilised; and
- ion exchange reaction may reverse and release exchanged metals.

#### 4.4 The Role of Microbial Activity

The microbial activity enhanced the removal of metals from the water in particular manganese. Manganese oxides were found on iron bacterium (*Leptothrix discophora*), green algae (*Ulpithix* sp), cyanobacteria, fungi/actinomycetes, protozoans and macrophytes at acid-drainage sites in USA (Robbins et al. 1999). These microorganisms catalyse the reaction of dissolved oxygen with manganese.

After almost one year the limestone neutralisation in the modified OLC was found to add as much or more alkalinity as fresh limestone if the sediment coating was removed by gentle shaking in the water. The alkalinity produced in November 2002 if the sediment was not removed from the limestone was 60% of that produced with fresh limestone. More aluminium and manganese but slightly less iron was removed when this coating was on the limestone compared to fresh limestone. The adsorption of metals to the coating on the limestone and microbial activity is the most likely reason for this. Manganese oxides have negative charge and large surface area and can adsorb large quantities of cations (Murray 1974). Ferric oxyhydroxides also exhibit high cation adsorption capacity (Hem 1985). Cravotta and Trahan (1999) documented the removal of iron, manganese, and trace metals in an oxic limestone drain for treatment of acidic drainage from a coal mine and suggested these same processes could be active.

Abiotic precipitation of manganese oxides will be slow at pH <9 (Hem 1985), however microbes can catalyse the manganese oxidation between pH 6.5 and 7.5 (Nealson 1983). From 14 December 2001 to 7 November 2002 the average daily pH was greater than 8 on 8 days (2.4% of the total days) and the pH was greater than 6 on 94 days (28.7% of the total

days) at water quality monitor B (Fig. 1). The microbial activity is still active on the limestone in November despite concerns that a pH less than 6 may be intolerable to microbial community (Hedin et al. 1994). The pH on or near the limestone surface could be greater than that of the bulk solution.

Aluminium does not produce usable energy for bacteria during oxidation and reduction (Robbins et al. 1996) because it is not redox sensitive (Nordstrom and Ball 1986). Robbins et al. (1996) suggested that bacteria could armour themselves with aluminium for detoxification or aluminium could use bacteria as a nucleation site due to the surface charge. Robbins et al. (1996) also suggested that when aluminium precipitates due to pH rise, the bacteria may adsorb to flocculants.

## 5 Conclusions

On balance, the OLC has been found to be an effective means of neutralising acidic discharge waters and removing metals from solution. It was constructed within an existing drainage channel and therefore was only designed to treat a portion of the water discharged. It is capable of treating flows in the initial period of the rainfall event and recession when the catching pump switches periodically on and off for a total of 33–40 min a day. A significantly larger OLC would be required to treat all the acidity and metals that can be discharged during episodic rainfall. However, the simplicity and low expense of the system are desirable features.

Beaker tests indicated that dissolved metals and thereby acidity were removed from ASS drainage water however, the longevity of the system will be reduced unless the limestone is periodically agitated to remove the sediment that has accumulated on its surface. Sediment accumulation is a greater problem than limestone armouring.

In addition to sediment accumulation on the surface of the limestone bed, metals precipitation occurred on the underlying limestone. The precipitation of manganese oxides were dominant, followed by aluminium then iron precipitates. The microbial activity and adsorption of metals to the existing coating are important in increasing the amount of alkalinity added and metals removed. The amount of dissolved metals, and thereby acidity, removed from

the water is increased on the armoured limestone with microbial activity, compared to fresh limestone. If sediment has accumulated on the limestone then the amount of alkalinity added may be less but dissolved metals may still be removed by adsorption or surface attachment (if pH is sufficiently high).

The likely major processes occurring in the modified OLC are:

- aeration and oxidation of ferrous iron to ferric iron (catchment pump);
- dilution during large rainfall events;
- dispersion due to the pond and roughness of the limestone;
- biotic precipitation/co-precipitation of manganese and iron oxyhydroxides;
- abiotic precipitation/co-precipitation of aluminium and iron oxyhydroxides, and gypsum;
- adsorption and ion exchange; and
- deposition of sediment.

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